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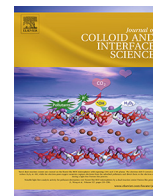
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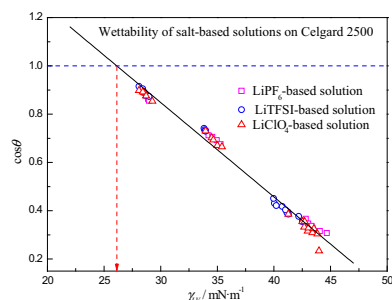


Regular Article

Wetting behavior of four polar organic solvents containing one of three lithium salts on a lithium-ion-battery separator

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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: The wetting behavior of an electrolyte solution on the separator, determined by contact-angle measurements, has a significant effect on the internal resistance of the battery and on its cycle life. The solvent, the lithium-salt type and its concentration may affect the wettability. However, few systematic studies address the effect of salt concentration on surface tension and contact angle.

Experiments: Surface tensions and advancing contact angles were measured for dimethyl sulfoxide (DMSO), propylene carbonate (PC), dimethyl carbonate (DMC), and a PC/DMC mixture (1:1 mass ratio) with various concentrations of a lithium salt (LiClO₄, LiPF₆, and LiTFSI) at 23 °C. Measurements were made by a Krüss Drop Shape Analyzer 100, with a video camera mounted on a microscope to record the drop image.

Findings: For DMSO, PC and PC/DMC, surface tensions increase by adding LiClO₄ or LiPF₆ but decrease upon addition of LiTFSI. For DMC, the lithium salts have little impact on the surface tensions. For each solvent, contact angles and adhesion energies follow the same trend as those for surface tensions. The TFSI- anion reduces the surface tension of the solvent, favoring good wettability of the separator. The optimal surface tension for wettability of Celgard 2500 is at or below 26.1 mN/m.

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1. Introduction

Lithium-ion batteries are efficient electrochemical-energy-storage devices used, for example, in mobile phones, electric vehicles, and for renewable energy storage [1–5]. These batteries contain a non-aqueous electrolyte solution and a microporous membrane to prevent an internal short circuit while allowing

Li⁺-ion transfer [6,7]. For efficient operation and ease of cell assembly, the salt-containing solvent should easily wet the separator because good wetting facilitates Li⁺-ion mass transfer. When the wettability of the separator is poor, the pores in the separator are not completely filled with liquid, causing high resistance for Li⁺-ion transport. The wetting behavior of an electrolyte solution on the separator may have a significant effect on the internal resistance of the battery as well as on its cycle life [8–10].

Wetting properties are determined by the contact angle [11]. Numerous studies show that insufficient wetting gives poor battery performance [12–16]. However, few systematic studies address the effect of salt concentration on surface tension and contact angle. This work presents a study of the surface tension and advancing contact angle for dimethyl sulfoxide (DMSO), propylene carbonate (PC), dimethyl carbonate (DMC), and a PC/DMC mixture (1:1 mass ratio) containing one of three lithium salts (LiClO₄, LiPF₆, and LiTFSI) at 23 °C. Salt molalities vary from zero to 0.8 M. Upon estimating dispersive and polar components of surface free energy for solid-vapor (separator-dried air) and for liquid-vapor (solution-dried air), Young's equation gives the free energy of the solid-liquid interface (separator-solution). Finally, Zisman's critical surface tension for Celgard 2500 was obtained.

2. Experimental section

2.1. Solvents and salts

Dimethyl sulfoxide (DMSO, ≥99.9%), propylene carbonate (PC, ≥99.5%), dimethyl carbonate (DMC, ≥99%), lithium perchlorate (LiClO₄, ≥99%), lithium hexafluorophosphate (LiPF₆, ≥97%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, ≥99%) were purchased from Sigma-Aldrich. All chemicals were dried before use. Karl-Fischer titration showed that the water content for each solvent is lower than 50 ppm. Electrolyte solutions with various lithium-salt molalities were prepared in a glove-bag with a dry-nitrogen atmosphere. The electrochemical separator is a 25 μm microporous monolayer polypropylene membrane (Celgard 2500).

2.2. Measurements

Surface tensions and advancing contact angles were measured using a Krüss Drop Shape Analyzer (DSA) 100, with a video camera (FOculus *t*-series CMOS) mounted on an ORIEL 25,010 microscope to record the drop image. The video signal was transmitted to a frame grabber, with the image acquisition and analysis performed on a computer, with DSA version 1.90.0.11 software. A transparent glass chamber keeps a dry atmosphere dried with drierite (≥98% CaSO₄; <2% CoCl₂).

In the advancing-contact-angle experiment, the syringe needle remains in the drop during the entire measurement as shown in Fig. 1. The tip of a needle with a diameter of about 2 mm is placed very near the solid surface. The drop is very slowly enlarged by adding liquid using a syringe pump. The contact angle initially

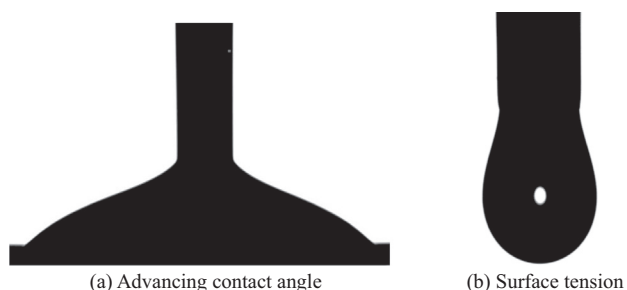


Fig. 1. Advancing contact angle and surface tension snapshots of solutions.

Table 1

Densities (ρ) and surface tensions (γ_{LV}) for water, PC, and DMC at 23 °C.

Liquid	$\rho/\text{kg}\cdot\text{m}^{-3}$		$\gamma_{LV}/\text{mN}\cdot\text{m}^{-1}$	
	Our data	Literature	Our data	Literature
H ₂ O	0.999	0.998[17]	72.35	72.31[21]
DMSO	1.100	1.097[18]	42.51	42.60[22]
PC	1.201	1.202[19]	41.28	41.39[23]
DMC	1.065	1.065[20]	28.55	28.60[20]

mN·m⁻¹: millinewton per meter.

increases, and then the drop starts to wander over the solid surface. The contact angle is measured as soon as the drop remains still or during its (slow) advance across the solid surface. For each system, the advancing-contact-angle measurement was performed about 6 times at different positions on the solid surface, and the average value was recorded. The uncertainties in the contact angles are less than 0.3°.

For surface-tension measurements, the pendant-drop method was used as indicated in Fig. 1. The solution was filled into a glass syringe, and then the syringe was fixed into the experimental equipment. A stainless-steel needle with an outside diameter of 1.81 mm was used to form the drops. When a liquid drop hangs from the syringe needle, this drop has a characteristic shape and size; these determine the interfacial tension. For each system, the surface-tension measurement was performed about 10 times. The uncertainty in the surface tension is less than 0.2 mN/m.

In the pendant-drop method, the density of the solution is required for determination of the surface tension. Densities were measured at 23 °C using a pycnometer and an analytical balance (Mettler AT261) with uncertainty ±0.1 mg.

To ensure reliability, the apparatus was first used to measure the densities and the surface tensions for water, DMSO, PC, and DMC. As shown in Table 1, our experimental data agree well with those reported in the literature.

3. Results and discussion

3.1. Experimental data

Table 2 present the density, surface tension, and advancing contact angle for DMSO, PC, DMC, and PC/DMC (1:1 mass ratio) with various lithium-salt molalities near room temperature (23 ± 1 °C). Fig. 2 illustrates how contact angle θ gives the wetting properties of a fluid on a separator surface. A large contact angle indicates poor wetting while good wetting is indicated by a small contact angle. The data show that dissolved lithium salts have a significant impact on wettability. Fig. 3 shows the effect of a dissolved lithium salt on the contact angle. For the same solvent at the same salt molality, different lithium salts show different contact angles. For DMSO, the contact angle of 0.4 M LiTFSI/DMSO (66.7°) is much lower than that of 0.4 M LiPF₆/DMSO (70.9°) or for 0.45 M LiClO₄/DMSO (71.6°). Similar results are obtained for PC, DMC and PC/DMC, indicating that the dissolved TFSI⁻ anion is better able to wet the separator than FP₆⁻ or ClO₄⁻ anion.

Fig. 4 shows surface tensions for DMSO with various lithium salts. The surface tension of 0.4 M LiTFSI/DMSO (41.23 mN/m) is lower than that of 0.4 M LiPF₆/DMSO (43.43 mN/m) or 0.45 M

Table 2

Surface tensions (γ_{LV}) and contact angles (θ) for water and diiodomethane at 23 °C.

Fluid	$\gamma_{LV}/\text{m}\cdot\text{Nm}^{-1}$	$\theta/^\circ$
H ₂ O	72.35	110.5
Diiodomethane	50.51	62.6

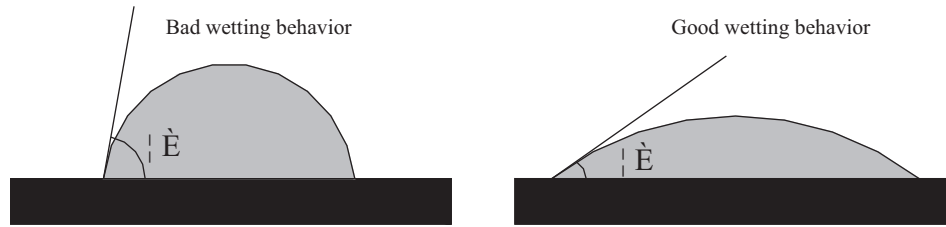


Fig. 2. Wetting behavior for a liquid on a solid surface.

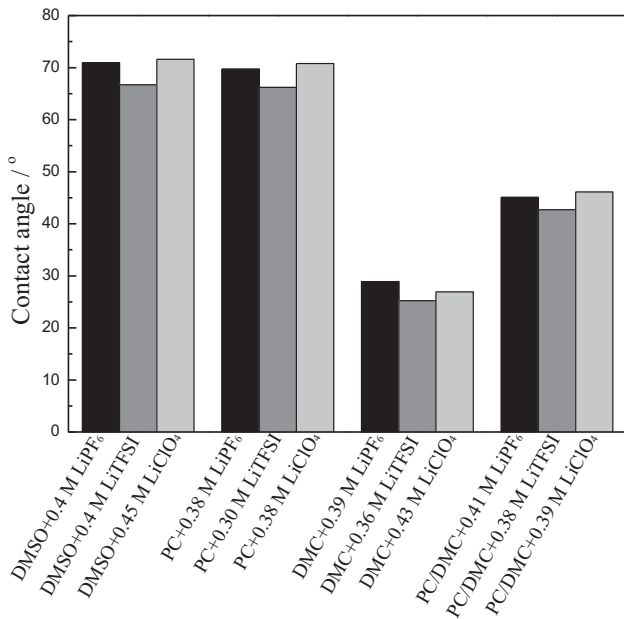


Fig. 3. Contact angles for lithium-salt solutions on a Celgard 2500 separator at 23 °C.

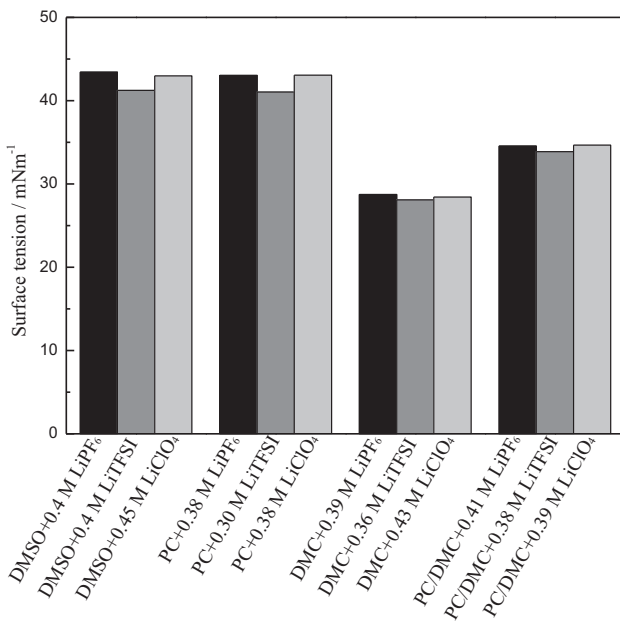


Fig. 4. Surface tensions for lithium-salt solutions at 23 °C.

LiClO₄/DMSO (42.99 mN/m). A low surface tension of the solution leads to a low contact angle. As shown in Fig. 5, with increasing lithium-salt concentration for each solvent, we observe different

trends of contact angle. For DMSO, PC and PC/DMC, the contact angles increase with rising concentration of LiClO₄ or LiPF₆, but decrease with rising concentration of LiTFSI. For DMC, the contact angle of DMC/lithium salt is lower than that of pure DMC at low concentration of lithium salt (less than about 0.4 M) but is higher than that of pure DMC when the molality exceeds about 0.4 M. As shown in Fig. 6, for each solvent, the trend of the surface tension with rising lithium salt molality is the same as that for the contact angle. The lower contact angles for LiTFSI-containing solutions may be due to the strong lyophobic nature of the perfluoroalkyl group -CF₃ in the TFSI⁻¹ anion. This lyophobicity may cause LiTFSI to adsorb on the separator [24].

3.2. Surface free energy

The interfacial properties of the separator affect the transport of electrolytes into the solid-liquid interface. As discussed in textbooks [25–27], the surface free energy of the solid surface cannot be directly obtained from standard experiments, but can be indirectly obtained from wettability data. The most commonly used method is first to estimate dispersive and polar contributions to the surface free energy.

The surface free energy between the solid and the vapor γ_{SV} is the sum of dispersive and polar contributions:

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \quad (1)$$

Similarly, for the surface free energy between the liquid and the vapor:

$$\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p \quad (2)$$

The Owens-Wendt equation was used to calculate the dispersive and polar parts of the surface free energy for solid-vapor and for liquid-vapor using two reference fluids. The Owens-Wendt equation is [28]:

$$\gamma_{LV}(1 + \cos\theta) = 2 \left(\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p} \right) \quad (3)$$

where the superscripts *d* and *p* refer to the dispersive and polar contributions, respectively. The subscripts *S*, *L* and *V* refer to the solid, liquid and vapor phases. To obtain the solid-vapor surface free energy, the dispersive and polar components between the solid and vapor (γ_{SV}^d and γ_{SV}^p) must be known; they can be calculated from data for two reference fluids. We selected water ($\gamma_{LV}^d = 21.8$, $\gamma_{LV}^p = 51 \text{ m}\cdot\text{Nm}^{-1}$) [29] and diiodomethane ($\gamma_{LV}^d = 50.8$, $\gamma_{LV}^p = 0 \text{ m}\cdot\text{Nm}^{-1}$) [30] for the two reference fluids, and then measured the surface tensions and advancing contact angles on Celgard 2500 separator for each reference fluid. Results are shown in Table 2. Knowing γ_{LV} , θ , γ_{LV}^d and γ_{LV}^p for the two reference fluids, we find the surface free energy for solid-vapor (between the separator and dried air; $\gamma_{SV} = 26.76$, $\gamma_{SV}^d = 26.76$ and $\gamma_{SV}^p = 0 \text{ m}\cdot\text{Nm}^{-1}$) from Eqs. (1)–(3). Knowing γ_{SV}^d , γ_{SV}^p , contact angle, and surface tension of the lithium-salt solutions, we then find γ_{LV}^d and γ_{LV}^p for each solution from Eq. (3).

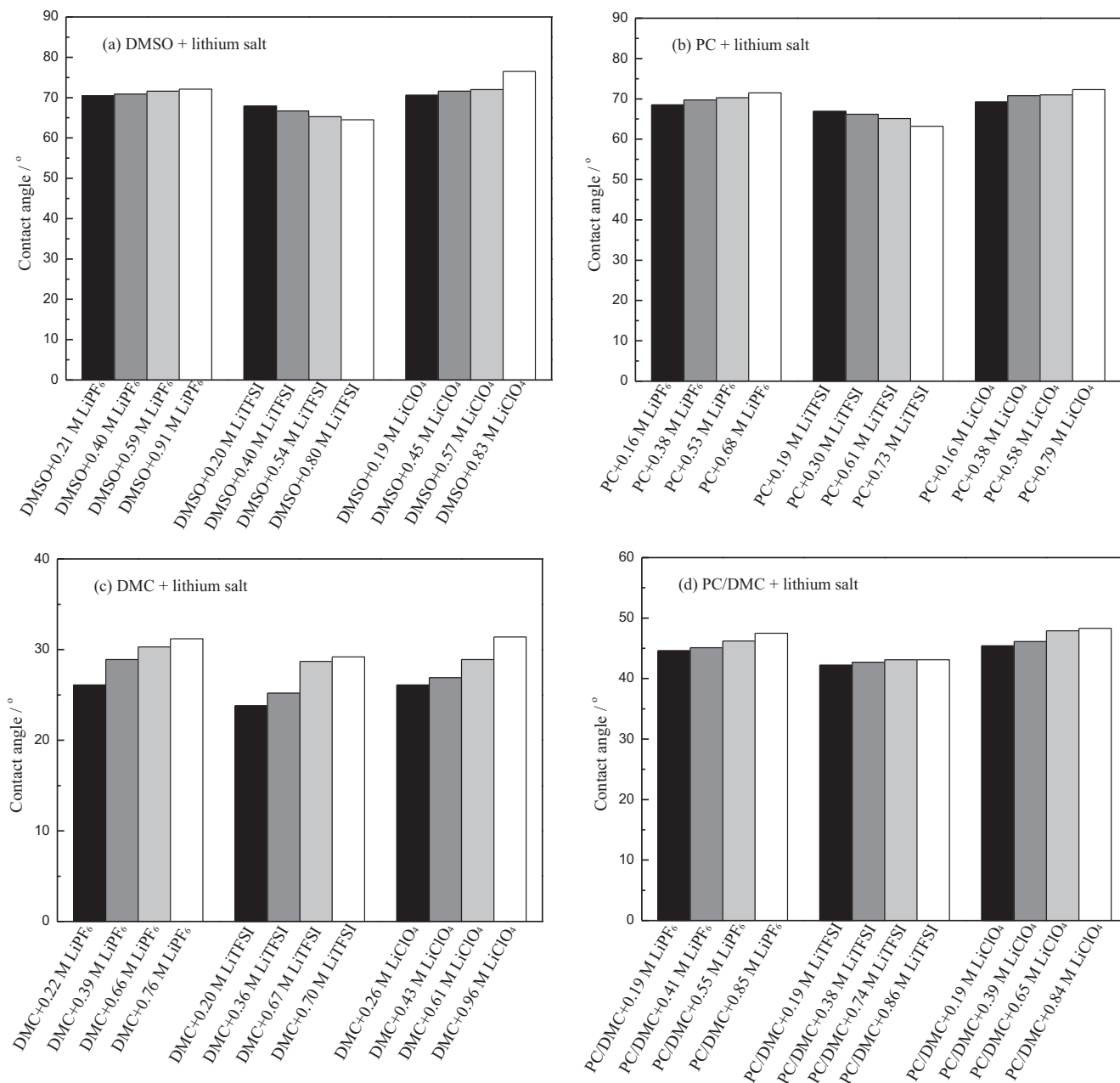


Fig. 5. Contact angles for solutions with various salt concentrations on a Celgard 2500 separator at 23 °C: (a) DMSO + lithium salt; (b) PC + lithium salt; (c) DMC + lithium salt; (d) PC/DMC + lithium salt.

The interfacial free energy between the solid and the liquid (γ_{SL}) was calculated using Young's equation [25–27]:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (4)$$

When the solid/liquid interactions from dispersion force only ($\gamma_{SV}^p = 0$), the work of adhesion is [29]:

$$I_{SL} = I_{SL}^d = \gamma_{LV} (\cos \theta + 1) = 2 \sqrt{\gamma_{SL}^d \gamma_{LV}^d} \quad (5)$$

γ_{LV}^d , γ_{LV}^p , γ_{SL}^d , and I_{SL} for the solutions with various lithium-salt molalities are given in Supplementary information. DMC exhibits the lowest contact angle indicating that DMC wets the separator better than the other solvents. As expected, DMC gives the lowest interfacial free energy γ_{SL} indicating good “compatibility” of DMC for the separator. Comparing the polar parts of the surface free

energies γ_{LV}^p for the liquids, DMSO shows the highest, followed by PC, PC/DMC and DMC. This trend demonstrates that the solvent with a lower polar part of surface free energy provides good compatibility with the polypropylene separator. Upon addition of LiTFSI, γ_{LV}^p and γ_{SL} decrease but an increase is observed upon addition of LiClO₄ or LiPF₆. For DMSO, PC and PC/DMC, γ_{LV}^p and γ_{SL} increase with rising concentration of LiTFSI, the higher the concentration of LiTFSI the better the wettability of the separator. Wetting is impaired by addition of LiClO₄ or LiPF₆. Owing to the relatively low γ_{LV}^p of DMC, no significant differences for γ_{SL} are observed at various lithium-salt concentrations, indicating that, for this solvent, lithium salts have little impact on the wettability of the separator.

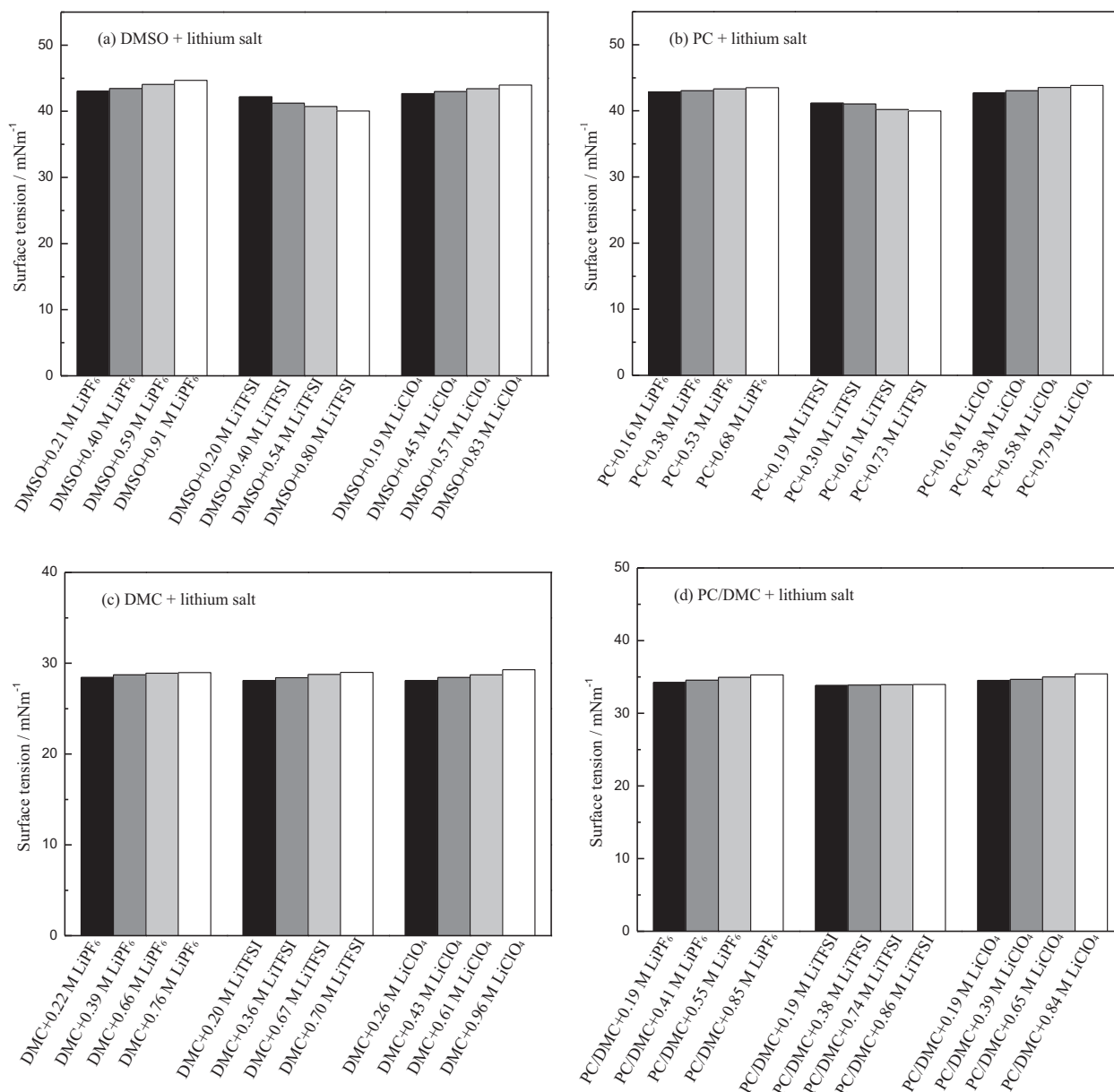


Fig. 6. Surface tensions for solutions with various salt concentrations at 23 °C: (a) DMSO + lithium salt; (b) PC + lithium salt; (c) DMC + lithium salt; (d) PC/DMC + lithium salt.

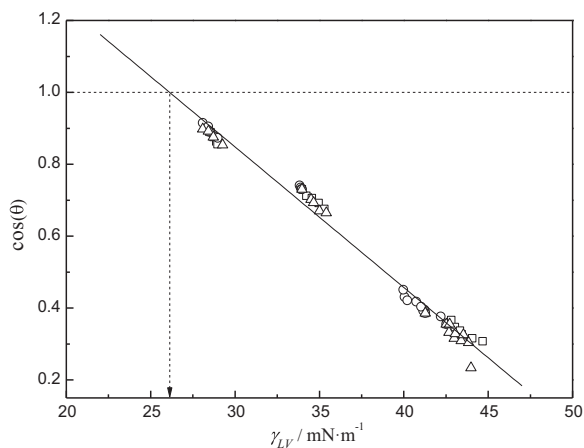


Fig. 7. Zisman's plot ($\cos\theta$ vs γ_{LV}) for solvent (DMSO, PC, DMC or PC/DMC) with various lithium-salt concentrations on a Celgard 2500 separator: solvent + LiPF_6 (□), solvent + LiTFSI (○), and solvent + LiClO_4 (△).

Along with the surface free energy, Zisman's critical surface tension has been widely used for characterization of a solid surface. The critical surface tension γ_c is defined as the intercept of the horizontal line, $\cos\theta = 1$, with the extrapolated straight-line plot of $\cos\theta$ against γ_{LV} as shown in Fig. 7. This intersection is the point where the contact angle is zero. A hypothetical test liquid having this γ_{LV} would spontaneously spread over the solid. Fig. 7 shows that the optimal surface tension for best wettability for Celgard 2500 is at or below 26.1 mN/m .

4. Conclusions

On the basis of the previous studies [12–16,31], the solvent, the lithium-salt type and its concentration may affect the wettability determined by the contact angle. However, few systematic studies address the effect of salt concentration on surface tension and contact angle. Toward better understanding the performance of an electrolyte/separator interface in a lithium-ion battery, surface

tensions and contact angles were measured for DMSO, PC, DMC, and PC/DMC mixture (1:1 mass ratio) with various lithium-salt (LiClO₄, LiPF₆, and LiTFSI) molalities on a Celgard 2500 separator. From the contact angle, surface tension, dispersive and polar components of surface free energy, the solid-liquid interfacial free energies were estimated using Young's equation. Liquids with low solid-liquid interfacial free energy and with low polar component of the surface tension are welcome to the separator. LiTFSI is more likely to show favorable separator wettability, compared to LiPF₆ and LiClO₄. The low surface tension resulting from the perfluorinated alkyls (-CF₃) terminal in the TFSI⁻¹ anion is responsible for favorable separator wettability. High concentrations of LiTFSI enhance separator wettability, but high concentrations of LiPF₆ or LiClO₄ impair separator wettability. Owing to relatively low polar component of the surface tension for DMC, lithium salts in that solvent have little impact on separator wettability. Ziman's critical surface tension for Celgard 2500 separator shows that the optimal surface tension for best wettability is at or below 26.1 mN/m. Further investigations on thermodynamic properties of the electrolyte-salt mixtures (such as vapor pressure, viscosity, conductivity etc.) are required to determine the relation between the wettability and various properties of electrolyte-salt mixture, so that fundamental data can provide development of the lithium-ion battery.

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